

Real-Time Detection of Trace Air Toxics in Exhaust of Combustion Systems Using Jet Resonance-Enhanced Multi-Photon Ionization–Time-of-Flight Mass Spectrometers

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The U.S. Environmental Protection Agency's (U.S. EPA) National Risk Management Research Laboratory (NRMRL) is applying laser-based technology, jet REMPI-TOFMS, for the real-time detection of trace amounts of hazardous air pollutants (HAPs). The technology has been developed in collaboration with SRI International and has been funded by the Department of Defense (DoD, Strategic Environmental Research and Development Program), the Department of Energy (Mixed Waste Focus Area), the U.S. Army (Program Manager for Chemical Demilitarization), and the U.S. EPA's ORD. Most techniques for sampling combustion sources for HAPs typically require a long sampling duration to exceed method detection limits (e.g., 1–3 hours), thereby excluding detection of pollutant levels during transient events, such as shutdowns or restarts. Jet resonance-enhanced multi-photon ionization (REMPI)–time-of-flight mass spectrometers (TOFMSs), on the other hand, can provide such data in real time (1 sec resolution). The technique consists of the laser-induced photoionization of molecules using REMPI. The resultant ions are separated en masse following extraction into a TOFMS. By changing the wavelength emitted from a tunable, pulsed laser source, a unique molecule-specific “fingerprint” spectrum can be obtained. When the spectrum is combined with the mass separation, one has a two-dimensional detection method with selectivity up to the isomer and isotopomer separation level, all in real time. The target analytes are introduced through a pulsed valve system, and the subsequent supersonic expansion (hence, “jet” REMPI) of the gas results in adiabatic cooling of the target analyte. Concentrations down to less than 1 ppb can be measured for numerous aromatics such as benzene, toluene, and polycyclic aromatic hydrocarbons (PAHs). The application of jet REMPI has also been extended to the near real-time detection of dioxin indicator compounds that correlate with toxicity. For such applications, an organic pre-concentration step can be used if the selected dioxin indicator compounds are below the real-time detection limit. Even in this case, concentration values are returned on the order of every 30 minutes compared with conventional extractive methods, in which the laboratory analysis typically requires weeks. The technology has been applied to the exhaust from a DoD diesel generator, a DoD turbine engine, and a commercial industrial boiler system. Real-time results that include transient events, such as cold starts and changes in loading as well as emission factors from regular operation conditions, can be determined. The jet REMPI-TOFMS results compare well with the conventional extractive, gas chromatography-based analyses.